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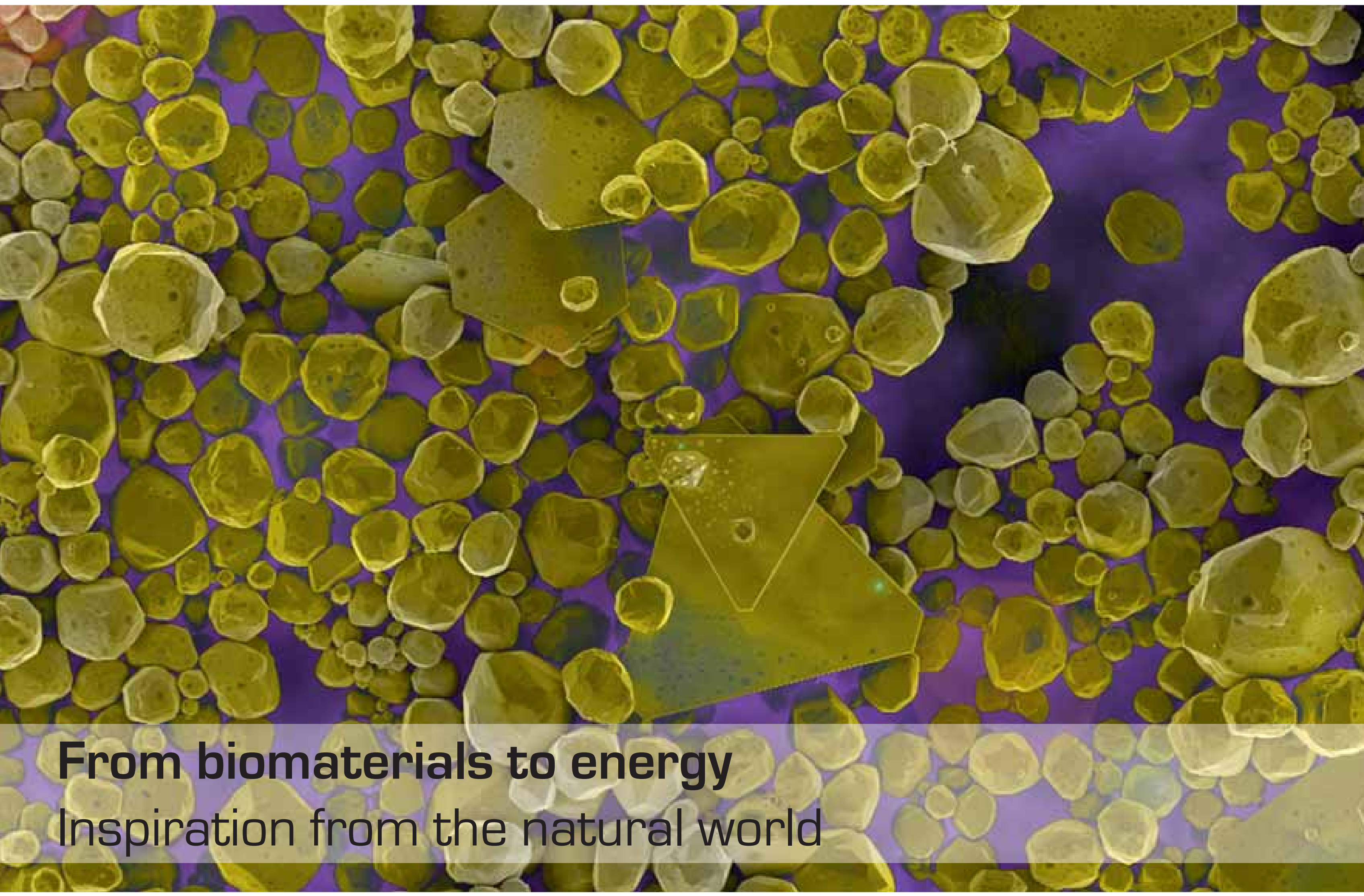

From biomaterials to energy

Inspiration from the natural world

Skin-inspired electronics

What can hydrogels do for the brain?

Catalysis for energy

Uncovered

Reliable and cheap SERS active substrates

Ordered *vs* disordered

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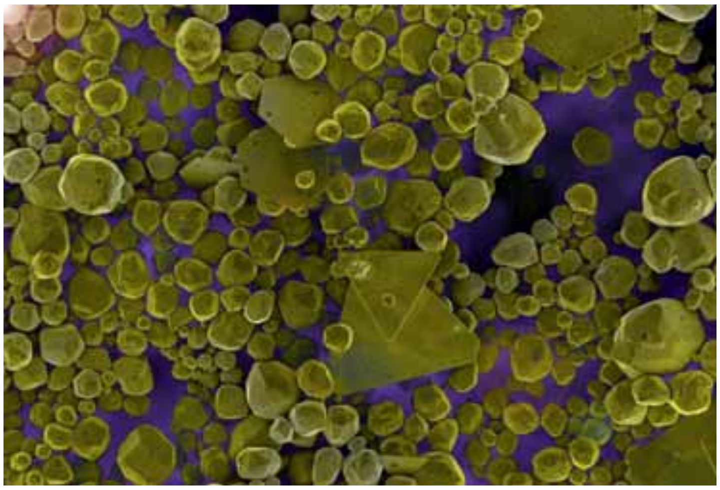

Raman spectroscopy is a label-free technique for the detection and structural analysis of molecular materials. Unfortunately, Raman signals are inherently weak, so a very low number of scattered photons are available for detection.

Surface Enhanced Raman Spectroscopy (SERS) is a useful method to amplify weak Raman signals by an increment of the apparent Raman cross-section of the analyte though the local amplification of the electromagnetic field in the close proximity of metal nanostructures caused by the excitation of localized surface plasmon resonances. Laser excitation resonantly drives the metal surface charges, creating highly localized plasmonic light fields at these photonic structures, which are known as hot-spots. Since the Raman signal is proportional to the intensity of the field, when a molecule is bonded, adsorbed or lies close to the enhanced field of a hot-spot, a huge increase in the Raman signal can be observed-usually of several orders of magnitude, consequently boosting the sensibility of the technique to concentrations as low as 10^{-18} M or even down to single molecule detection [1,2].

A key parameter to take into account in SERS experiments is the choice of the enhancing substrate. SERS substrates can be roughly classified into three main classes:

1. *Metallic electrodes*: These played an important role in the development of SERS. However, their importance has decreased substantially due to development of substrates with higher amplification power.
2. *Metal nanoparticles in solution:* Colloids have been and still are very important in the development of the technique. The liquid media is a useful aid to drive target molecules to the plasmonic surfaces, but sometimes the analyte is insoluble or incompatible with the liquid media, representing a problem for its easy and general application.
3. *Nanostructured substrates:* These may be obtained by two main methods: (a) deposition of metal nanoparticles from colloidal solutions by drying or evaporation of solvent onto appropriate substrates, or (b) fabrication of nanostructured metal surfaces, taking advantage of micro and nano-fabrication techniques.

The main obstacle limiting the use of SERS as an everyday and routine lab technique is the lack of suitable substrates. Despite the high number of publications and patents where new active materials are proposed, commercial substrates are still scarce and often expensive and quite unstable, e.g. requiring storage in controlled atmospheres and careful handling to maintain their enhancement properties.

The image featured on this issue's cover was taken with a field emission scanning electron microscope (FE-SEM Zeiss Ultra-Plus, at 1.5 kV with an in-lens secondary electron detector) and depicts a nanostructured substrate obtained by drying a colloidal solution of gold nanoparticles on a silicon wafer. These substrates are attractive because of the beauty and variety of morphologies, but also due to the simple synthesis of the nanoparticles and the ease of the fabrication process; however, they are often hindered by the limited control of size, shape and distribution of nanoparticles, which do not contribute to reproducible measurements.

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On the other hand, in the last decade it has been possible to design and built an increasing number of nanostructured metallic structures, ranging from nanodots to three dimensional scaffolds with potential applications as SERS substrates. In particular, a high level of freedom and control of shape, size and spatial distribution of the nanostructures may be obtained by lithographic or direct writing techniques, even though the expense of the production process caused by the high cost of machines, materials, masks, time of fabrication and low throughput of conventional techniques is strongly limiting their diffusion. In this sense, promoting a wider use of SERS, both in the lab and in real world applications, is conditioned by a reduction in production costs of SERS substrates.

We propose a simple two step fabrication process for cheap and reliable SERS substrates. The first stage comprises the fabrication of structured surfaces on polymers by ultra-violet nano-imprint lithography (UV-NIL) [3], following by deposition of the active metal layer covering the structured polymeric structure.

As a material for the NIL process we have synthesized a fluorinated elastomer that operates as a reliable and highly efficient photo-curable resist [4]. This material, a tetrafunctional urethane methacrylate perfluoropolyether, is a low viscosity liquid and forms a high modulus elastomer which can reproduce micro and sub 10 nm features with large aspect ratios, high fidelity and resolution and can be used for manufacturing large area structures by using wafer size stamps or roll to roll UV-NIL methods. Polymerization takes just a few seconds, does not involve solvents, heating steps, and does not produce residues. The second and final step, deposition of a metallic layer (by evaporation, sputtering or electroplating) on top of the structured polymeric replica provides control of parameters like thickness, rugosity and also metal selection (not only gold and silver were tested, aluminium and iridium produce very good results [5]).

The SERS active substrates obtained by this procedure overcome the usual limitations of lack of control and high cost of conventional substrates, and experimental results show a comparable or higher enhancement signal than that obtained with expensive commercial substrates.

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Further reading

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